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TITLE: PRESSURE-SENSITIVE ADHESIVE COMPOSITION
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TITLE OF THE INVENTION: Pressure-sensitive adhesive composition

CLAIMS

1. A pressure-sensitive adhesive composition is characterized by the fact that is consisted of (A) photopolymerizable oligomer made of alpha-olefin carboxylate which can be bonded in a pendant form by an addition reaction with functional groups which are present within acryl group copolymer, (B) monomer or oligomer having at the least one vinyl group or acryloyl group as a dilutant, and shows a photopolymerizing capability, (C) polyisocyanates, melamine. formaldehyde resin, or epoxy resin which are effective as corsslinking agents, (D) photocuring reaction initiator and sensitizer, and (E) tackifier.

DETAILED EXPLANATION OF THE INVENTION

[Field of industrial application]

This invention pertains to a pressure-sensitive adhesive composition which is used as various tapes including pressure-sensitive adhesive tapes, surface protective, and semiconductor carrier tapes, and other tack labels.

[Prior art]

According to ester polyacrylate or ester acrylate copolymers which are widely used as pressure-sensitive adhesive agents at this time, in order to attain the prescribed adhesive features, that is to say, in order to display adhesive force to adherents and cohesive force of adhesive agent itself, it is necessary to use such polymers showing a fairly high molecular weight as well as high viscosity; and to do so, a method to dissolve in an organic solvent to give a solution form to coat on a substrate, and then, to evaporate the solvent to allow resin components to remain on the substrate surface is generally practiced. According to this method, various installation and equipment set up to attain said removal and collection of organic solvents which are evaporated at large volume during such manufacturing process force to invite economical inconveniences from the standpoint of meeting requirements on the pollution prevention and energy saving.

On the one hand, according to the Japanese patent Kokai Sho 58[1983]-118872, a technology to prepare pressure-sensitive adhesive tapes by an addition reaction of ester acid having acryl group double bonding with glycidyl methacrylate to subject to an esterification, and then, by applying a curing reaction with electron beam is disclosed; and furthermore, according to the Japanese patent Kokai Sho 58[1983]-118872, a technology to add glycidyl methacrylate to pressure-sensitive adhesive composition (contains pentenyl group) having the main component of low molecular weight acryl copolymer in absence of organic solvent, and then, to cure this with an electron beam irradiation is disclosed; however, equipment cost becomes high for said curing by electron beam which is not satisfactory from the standpoint of economy.

[Subjects solved by this invention]

As explained above, according to the conventional technologies, no pressure-sensitive adhesive composition which either does not use or hardly uses organic solvents requiring an evaporation during manufacturing process has not yet been reported; and furthermore, no economical method to realize a curing reaction has been available; and they have been remaining as subjected which need to be solved.

[Measures used to solve the subjects]

In order to solve above-explained subjects, this invention uses a measure to prepare a pressure-sensitive adhesive agent composition consisted of (A) photopolymerizable oligomer made of alpha-olefin carboxylate which can be bonded in a pendant form with functional groups which are present in acryl group copolymer by an addition reaction, (B) monomer or oligomer having at the least one vinyl group or acryloyl group which shows photopolymerization capability as dilutant, (C) polyisocyanates, melamine, formaldehyde, or epoxy resin which are effective and crosslinking agents, (D) photosetting reaction initiator or sensitizer, and (E) tackifier. This invention is further explained in detail below.

First of all, the photopolymerizable oligomer (A) of this invention includes monomers of alkyl ester methacrylate with 6 to 12 carbon atoms such as hexyl acrylate, n-octyl acrylate, isooctyl acrylate, 2-ethyl hexyl acrylate, dodecyl acrylate, decyl acrylate, or monomers with less than 5 carbon atoms such as pentyl acrylate, n-butyl acrylate, isobutyl acrylate, ethyl acrylate, methyl acrylate, or methacrylates which are similar to above-explained examples may be mentioned. As for the recommended application rate of such alkyl ester acrylates and alkyl ester methacrylates explained above, it is preferable when it is generally 10 to 90 weight % (the term % hereafter all refers to as weight %); and appropriate adjustment of glass transition temperature may be made by combining monomers of alkyl group

with 6 to 12 carbon atoms and monomers of alkyl group with less than 5 carbon atoms. At this time, when monomers with less than 5 carbon atoms are used at large volume, glass transition point becomes high, and it is not appropriate and desirable as a pressure-sensitive adhesive agent. Furthermore, as such copolymerizable vinyl monomers which uses alkyl group with 6 to 12 carbon atoms at large volume and can be partially substituted with alkyl group with less than 5 carbon atoms, monomers including vinyl acetate or styrene acrylnitrile showing 30 to 106°C glass transition point may be mentioned; and rate of substitution should be less than 5 weight %. In addition, among the compounds having functional groups, glycidyl acrylate, glycidyl methacrylate, and allyl glycidyl ether are recommended. furthermore, as for the alpha-olefin anhydrous carboxylate, maleic acid anhydride, fumaric acid anhydride, or phthalic acid anhydride may be mentioned. The monomers having above-explained functional groups and alpha-olefin anhydrous carboxylate may be set as 1 to 80 % and 1 to 40 % respectively to the fact that said alkyl ester acrylates or alkyl ester methacrylates being 10 to 90 %.

The organic solvents which use such monomers as raw material during manufacturing operation of acryl group oligomers, the ones of ketone group, ester group, alcohol group, and aromatic group may be used. Among said examples, solvents (toluene, ethyl acetate, isopropyl alcohol, benzene, methyl cellosolve, ethyl cellosolve, acetone, methyl ethyl ketone) which show 60 to 120°C boiling point and are generally of good solvents for acryl group oligomer are recommended. Furthermore, as agents which initiates solution polymerization, radical initiators of azo b's group or organic peroxide group may be used; and although there are no special restriction placed, alpha, alpha'-azobis isobutyl nitrile or benzo peroxide are generally used. In addition, during manufacturing operation of photopolymerizable oligomers of acryl group, solution polymerization explained above is generally used; however, no problems are noted when a bulk polymerization or suspension polymerization is used; and in any case, as the acryl group oligomers of which invention which are provided after removal of solvents, the ones showing -70 to +10°C, or more preferably, -60 to 0°C glass transition temperature are recommended from the standpoint of pressure-sensitive adhesive property, heat resistance as well as solvent removal. When adjustment of molecular weight is required, solvents of mercaptan group or carbon tetrachloride group may be used.

The examples of monomers containing vinyl groups which can be added to the epoxy group contained in the acryl group copolymer prepared in above-explained manner include acrylic acid, methacrylic acid, maleic acid, fumaric acid; and open-ring reaction of epoxy group is carried out by compounding vinyl group at chemical equivalence to the epoxy group at lower than the boiling point of the solvents. At this time, it is all right to use catalysts or polymerization inhibitors as needed. Furthermore, progress state of the reaction may be judged by measuring the acid value of the reaction group to cease the reaction when oxidation reaches 0 point. Although amine group or ammonium chloride group may be used as catalysts, more concretely, amines such as triethyl amine, tributyl amine, dimethyl amino ethanol, diethyl amino ethanol, methyl amine, ethyl amine, n-propyl amine, isopropyl amine, 3-methoxy propyl amine, butyl amine, allyl amine, hexyl amine, 2-ethyl hexyl amine, or benzyl amine; and ammonium chlorides group including triethyl benzyl ammonium chloride may be mentioned; and when using these as catalysts, they may be compounded with vinyl group containing monomer at 0.01 to 20.0 % range. Furthermore, as polymerization inhibitors, hydroquinone, hydromonomethyl ether, 2,6-di-t-butyl hydrotoluene may be used; and when using these, it should be set as 0.01 to 5.0 % based on vinyl group containing monomer.

As explained above, it is possible to attain a photopolymerizable oligomer (A) having carboxyl group and hydroxyl group as functional groups by opening rings of epoxy group to carry out hydrolysis by adding above-explained amine group catalysts and minimum amount required to acryl group copolymers to which vinyl group and carboxylic acid anhydride are induced.

Then, the monomer or oligomer (B) having at the least one vinyl group or acryloyl group showing photopolymerization capability of this invention must work as dilutants of said acryl group photopolymerizable oligomer (A) and show low viscosity when in a solution state; and they may be selected from among the following 4 groups; and it is preferable that the application rate of these is determined according to the glass transition point of entire system so not to inhibit the pressure-sensitive adhesive property; and in general case, guide line target may be set as a group 5 to 95 %, b group 5 to 95%, c group 5 to 95 %, and d group 5 to 50 %:

(a) Monomers of alkyl ester acrylate or alkyl ester methacrylate:

methacrylates including acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethyl hexyl acrylate, nonyl acrylate, n-hexyl acrylate, stearyl acrylate, isodecyl acrylate, phenoxy ethyl acrylate, lauryl acrylate, ethoxy ethyl acrylate, methoxy ethyl acrylate, N,N-dimethyl amino ethyl acrylate, N,N'-diethyl amino ethyl acrylate, and their equivalents; and glycidyl methacrylate, 2-hydroxy ethyl acrylate, 2-hydroxy propyl acrylate, 2-hydroxy ethyl methacrylate, 2-hydroxy propyl methacrylate, benzyl acrylate, cyclohexyl acrylate, dicyclopentenyl acrylate, N-vinyl pyrrolidone, ethyl carbitol acrylate, styrene, vinyl acetate,

(b) diacrylates or dimethacrylates:

1,3-butane diol acrylate, 1,4-butane diol diacrylate, 1,6-hexane diol diacrylate, polyethylene glycol (#200) diacrylate, polyethylene glycol (#400) diacrylate, polyethylene glycol (#600) diacrylate, diethylene glycol diacrylate, neopentyl glycol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate, hydroxy bivaric acid ester neopentyl glycol diacrylate, trimethylol propane diacrylate, bis(acryloxy ethoxy) bisphenol A, bis(acryloxy ethoxy) tetrabromobisphenol A, 1,3-bis(hydroxy ethyl) 5,5-dimethyl hydantoin 3-methyl pentane diol diacrylate, 1,6-hexane diol diacrylate, neopentyl glycol diacrylate, tripropyl glycol diacrylate, propylene glycol (#400) diacrylate, 2,2-bis[4-(acryloxy diethoxy)phenyl] propane or methacrylates equivalent to these ,

(c) triacrylates or trimethacrylates:

trimethylol propane triacrylate, pentaerithritol triacrylate, tri(dihydroxy ethyl) isocyanate pentaerithritol monohydroxy pentaacrylate, tetramethylol methane triacrylate, tetramethylol methane tetraacrylate, dipentaerithritol hexaacrylate, or methacrylates equivalent to these ,

(d) urethane acrylates, epoxy acrylates, or methacrylates equivalents to these:

bifunctional urethane acrylate, tetrafunctional urethane acrylate, hexafunctional urethane acrylate, epoxy acrylate or methacrylates equivalent to these,

According to this invention, because acryl group copolymers tend to lack cohesive force, crosslinking agent (C) which can easily react with the functional group within said acryl group copolymer is used; and as such crosslinking agent, combinations of hydroxyl group, carboxyl group and polyisocyanates, carboxyl group and melamine formaldehyde resin, epoxy group and carboxyl group, or carboxyl group and polyvalent metal salt are effective; and for instance, polysiocyanates, melamine formaldehyde resin melamine alcohol modified resin (methoxy butoxy modified melamine resin), or epoxy resins may be mentioned.

Furthermore, according to this invention, in order to further increase high molecular weight of monomer, or oligomer (B) having at the least one vinyl group or acryloyl group which shows photopolymerization capability explained above, initiators and sensitizers (D) are used; and initiators of photopolymerization reaction include carbonyl compounds such as acetophenones, benzophenones, Michler ketones and benzoin, sulfur compounds such as tetramethyl thiuram monosulfide or thioxanethones, and other azo compounds may be used; and as sensitizers which promote the effect of initiators, n-butyl amine, di-n-butyl amine, tri-n-butyl phosphine, allyl thiourea, triethyl amine, and diethyl amino ethyl methacrylate may be mentioned. In general, when photoinitiators and sensitizers are jointly used, it is well known that crosslinking (curing) reaction is promoted; and the application rate of these initiators and sensitizers are preferable when it is 0.01 to 20.0 % range based on the oligomer having said photopolymerization capacity. The reason for such range is due to that when it is as small as less than 0.01 %, addition effect cannot be anticipated; and on the other hand, when it is as large as more than 20.0 %, curing speed becomes too great, and is not desirable.

Furthermore, it is preferable when such photopolymerization reaction is carried out by irradiation of UV rays (180 to 460 nm wavelength) generated from mercury arc, low pressure, medium pressure, high pressure, or super high pressure mercury lamp; however, as for the UV ray irradiation, it is necessary to avoid the hindrance by oxygen radicals which are generated from air under atmospheric environment, it is recommended to substitute the atmosphere with either inert gas or to cover the reaction system with a film to block off said air.

In addition, according to this invention, it is necessary to maintain an ideal level of pressure-sensitive adhesive force from the standpoint of increasing internal cohesive force by high molecular weight conversion reaction explained above to achieve balance among heat resistance feature, pressure-sensitive adhesive force, and cohesive force; and therefore, tackifiers (E) which are generally used are added. As for such tackifiers, natural resins including rosin group resins such as gum rosin, tall oil resin, wood rosin, rosin hydrate, or rosin ester and terpene phenol resin may be mentioned; and as synthetic resins, petroleum oil cumarone, indene resin, styrene resin, phenol group resin, and xylene group resin may be mentioned.

[Action]

As explained above, according to this invention, organic solvents are used only for acryl group when photopolymerizable oligomer (A) is adjusted with a solution polymerization; however, during a process which initiates photocrosslinking reaction by mixing acryl group photopolymerizable oligomer (A), dilutant consisted of monomer or oligomer which shows photopolymerization capability (B), and crosslinking agent (C) and sensitizer and other additives (D) and (D), solvents which require evaporation and collection are not used at all; and monomers or oligomers which are used as dilutants may be all converted to high molecular weight.

[Application examples]

APPLICATION EXAMPLE 1

400 g toluene was charged in a 2 L four-mouth flask equipped with a cooler, dropping funnel, and thermometer; and to this, while a mixture solution consisted of 360 g 2-ethyl hexyl acrylate, 29.4 g maleic acid anhydride, 85.2 g glycidyl methacrylate, and 4.8 g benzoyl peroxide was dropped through a dropping funnel by taking about 2 hours, it was reacted for 8 hours at 100 to 110°C temperature. Then, 43.2 g acrylic acid, 1 g hydroquinone, and 10 g triethyl benzyl ammonium chloride were added; and ester addition reaction was carried out for 8 hours at the same temperature. At the point when acid value became lower than 3, reaction was ceased; and to this, 6 g water and 2 g triethyl amine were added to carry out hydrolysis; and then, nonreacted water was removed of the system along with toluene to set the residual solvent to less than 1% to give acryl group photopolymerizable oligomer (A). To 100 g of this acryl group photopolymerizable oligomer (A), as an oligomer showing photopolymerization capability which is the dilutant (B), 20 g of trimethylol propane triacrylate (NK ester A-TMPT made by Shin Nakamura Kagaku Kogyo K.K.), and as photopolymerization reaction initiator, benzyl dimethyl ketal (Irgacure 651 made by Japan Ciba Geigy K.K.) 5 g, and as sensitizer, 5 g diethyl amino ethyl methacrylate, and as crosslinking agent (C), 5 g polyisocyanate (Colonate L made

by Nippon Polyurethane K.K.), and as tackifier (E), 20 g terpene phenol resin (Polystar T-115 made by Yasuhara Yushi K.K.) were added and mixed to give a resin composition; and this was coated on a polyester film surface with 20 μ m thickness to give 20 μ m coating weight; and this was irradiated by using a UV ray irradiation machine (30W) from 10 cm distance. The irradiation dosage was 450 mJ. A polyester pressure-sensitive adhesive tape was prepared in above-explained manner, and this was measured for its pressure-sensitive adhesive force (g/in) and holding force in accordance to JIS-Z0237; and obtained results are shown in the Table below.

Table

	application examples				comparative
	1	2	3	4	example
measured values:					
pressure-sensitive adhesive force (g/in)	100	80	250	150	1520
holding force (mm)					
40°C, 1 hour	0	0	0	0	0.5

APPLICATION EXAMPLES 2 THROUGH 4:

In the application example 2, instead of maleic acid anhydride of the application example 1, 29.4 g phthalic acid anhydride was used; and in the application example 3, instead of acrylic acid of the application example 1, 25.8 g methacrylic acid was used; and in the application example 4, instead of trimethylol propane triacrylate of the application example 1, nonyl phenoxy ethyl acrylate 20.0 was used; and they are prepared as polyester pressure-sensitive adhesive tapes in the same manner as explained in the application example 1; and they were measured for their pressure-sensitive adhesive force and holding force. Results are shown in the Table above.

COMPARATIVE EXAMPLE:

An acryl group low molecular weight copolymer was prepared in the same manner as explained in the application example 1 by adding 0.5 parts polyisocyanate (Colonate L) as a crosslinking agent to the solution. polymer used when adjusting the acryl group copolymer in the application example 1; and without applying other operation which follow, it was coated on a polyester (20 μ m) surface to give 20 μ m film thickness; and this was measured for its pressure-sensitive adhesive force and holding force in the same manner as explained in the application example, and results are shown in the Table above.

When above-explained application examples 1 through 4 and comparative example are compared, as it may be clear from the Table, holding force feature is noted to be better.

[Effect]

According to this invention's pressure-sensitive adhesive composition, because it does not or hardly uses organic solvents which require evaporation during manufacturing process, various equipment installation required from the standpoint of pollution prevention or energy saving on the organic solvent which are practiced in conventional technologies is not required to be referred to as economically useful. And therefore, the significance of this invention may be judged large.

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